Level Kinetic Approach in the Case of Strong Vibrational Nonequilibrium for a Pure Diatomic Gas

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Abstract: We present in this report a mathematical modelization of a pure gas flow in strong vibrational nonequilibrium. The model is deduced from the kinetic theory by the generalized Chapman-Enskog procedure. The transport coefficients are solutions of complex systems obtained in a general framework. Simpler systems are deduced from physical approximations and may be solved numerically at a low computational coast.

Key-words: Vibrational nonequilibrium, Chapman-Enskog, transport coefficients, systems.

(Résumé : tsvp)

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Approche cinétique par niveaux dans le cas d'un diatomique pur en fort déséquilibre vibrationnel.

Résumé : Nous proposons dans ce rapport un modéle mathématique pour les écoulements en fort déséquilibre vibrationnel, pour un gaz pur. Le modèle est déduit de la théorie cinétique des gas par la méthode de Chapman-Enskog généralisée. Les coefficients de transport sont solutions de systèmes complexes obtenus dans un cadre très général. Différentes approximations physiques permettent d'en déduire des systèmes simples que l'on peut résoudre numériquement pour un faible cout.

Mots-clé : déséquilibre vibrationnel, Chapman-Enskog, coefficients de transport, systèmes.

1 Introduction

In simulations of hypersonic flows, the one-temperature or multi-temperature models are commonly used [1], [2], [3], [4]. These models assume that the population of each vibrational level is described by a steady-state distribution, at the gas temperature in the case of equilibrium between all the degrees of freedom, or at a vibrational temperature in the case of vibrational nonequilibrium. But this assumption is not always valid. In particular, in a short relaxation zone behind the shock wave, where the vibrational distribution is strongly disequilibrated and can not be described by a steady-state distribution. Such flows are characterized by a mean vibrational collision time of the same order as the characteristic time of the flow and much greater than the mean translational and rotational collision times. It is important therefore to consider the population of each vibrational energy level as an unknown and to use the so-called level approach.

Various attemps have allready been made to study real gas flows using the level by level approach. Among the most recent, we may mention works on vibrational-chemical coupling behind a shock wave [5], [6], [7], [8], [9], [10], on expanding flows and nozzles [11], [12], on a nonequilibrium boundary layer near re-entering bodies [13], [13], [14] and on shock layer [15].

Following the level kinetic approach, the resulting macroscopic system has been derived in [16] in the case of a reacting gas mixture, including strong chemical nonequilibrium. In this paper, we will restrict our attention to a pure gas and, using notations of [16], recall the main results of the generalized Chapman-Enskog method. Then, we derive general systems to compute the transport coefficients: the shear and bulk viscosity, the thermal conductivity, diffusion and thermal diffusion. The complexity of inelastic collision cross sections prevent any computation without additional approximations. Thus, we propose approximations in order to obtain solvable systems. In this aim, we consider approximations used by [17], in the case of a gas mixture, assuming that the molecules at the different vibrational energy levels behave as molecules of different species. The resulting systems are formally similar to those derived in [18] for polyatomic gas mixtures.

2 Chapman-Enskog's zero order solution

We consider the semi-classical Boltzmann equation associated to the distribution function $f_{ij}(\mathbf{r}, \mathbf{u}, t)$, where the subscripts i and j denote rotational and vibrational energy levels respectively and the arguments denote the velocity $\mathbf{u}$, the space co-ordinate $\mathbf{r}$ and the time t. That equation is written as

$$\frac{\partial f_{ij}}{\partial t} + \mathbf{u}\frac{\partial f_{ij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{ij}^{rap} + J_{ij}^{sl}. \tag{1}$$

The collision operators J_{ij}^{rap}, J_{ij}^{sl} simulate rapid and slow processes, respectively. The parameter $\varepsilon = \tau_{rap}/\tau_{sl}$ is the ratio of the mean collision time of the frequent and rare collisions. The parameter ε is small under the hypothesis that

$$\tau_{rap} << \tau_{sl} \sim \theta, \tag{2}$$

where θ is a characteristic time of the flow. Assuming strong vibrational nonequilibrium, we may write $J_{ij}^{rap} = J_{ij}^{el} + J_{ij}^{r}$, $J_{ij}^{sl} = J_{ij}^{vibr}$, where collision integrals J_{ij}^{el}, J_{ij}^{r}, J_{ij}^{vibr}, correspond to elastic collisions and those including rotational and vibrational energy transfers respectively. The collision operator for rapid processes may be written as

$$J_{ij}^{rap} = \sum_{klj'l'} \int \left(f_{ij'} f_{kl'} \frac{s_j^i s_l^k}{s_{j'}^i s_{l'}^k} - f_{ij} f_{kl} \right) g \sigma_{ijkl}^{j'l'} d^2\Omega d\mathbf{u}_1, \tag{3}$$

where $\sigma_{ijkl}^{j'l'}$ is the inelastic cross-section of the collision leading to the change of translational and rotational energy, $\mathbf{g}$ is the relative velocity of modulus g, $d^2\Omega = sin\chi d\varepsilon d\chi$ is the solid angle, χ and ε are the polar and azimuthal deflection angles, and s_j^i is the statistical weight of rotational

energy level j for a molecule in vibrational level i. This integral describes the elastic collisions in the case $j = j'$, $l = l'$.

The collision integral J_{ij}^{vibr} includes VT and VV processes. Here, TRV processes are neglect because their probability is very small.

Following the Chapman-Enskog method, the distribution function $f_{ij}(\mathbf{r}, \mathbf{u}, t)$ is expanded in a power series of the parameter ε ($\varepsilon << 1$). The zero order solution is obtained solving the equation $J_{ij}^{rap}(f_{ij}^{(0)}, f_{ij}^{(0)}) = 0$. The solution represents the Maxwell-Boltzmann distribution function for translational and rotational degrees of freedom and is given by

$$f_{ij}^{(0)} = \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{n_i}{Z_i^r} s_j^i exp\left(-\frac{m}{2kT}(\mathbf{u}-\mathbf{v})^2 - \frac{\varepsilon_j^i}{kT}\right), \tag{4}$$

where m is the molecular mass, k is the Boltzmann constant, T is the gas temperature, $\mathbf{v}$ is the macroscopic velocity, ε_j^i is the rotational energy of the molecule at the vibrational level i and rotational level j, n_i is the nonequilibrium population of the vibrational level i, Z_i^r is the rotational partition function

$$Z_i^r = \sum_j s_j^i exp\left(-\frac{\varepsilon_j^i}{kT}\right). \tag{5}$$

Distribution (4) is obtained classically, knowing that the invariants of any collision are the mass $\psi_{ij} = 1$, the momentum $\psi_{ij}^{\nu} = mu_{\nu}$, $\nu = 1, 2, 3$, the total energy $\psi_{ij}^{e} = mu^2/2 + \varepsilon_j^i$, and, under condition of slow vibrational exchange, $\psi_{ij}^{\lambda} = a_i$, $\lambda = 1, ..., N$ (N is the number of vibrational energy levels), where a_i is a variable independent on the velocity and rotational energy level j and arbitrary dependent on i. The peculiarity of the generalized Chapman-Enskog method is that the zero order distribution function is already nonequilibrium.

The macroscopic parameters of the flows are defined as moments of the distribution function $f_{ij}(\mathbf{r}, \mathbf{u}, t)$. Thus we write

$$\sum_j \int f_{ij}^{(0)} d\mathbf{u} = \sum_j \int f_{ij} d\mathbf{u} = n_i, \qquad i = 1, ...N, \tag{6}$$

$$\sum_{ij} \int \mathbf{u} f_{ij}^{(0)} d\mathbf{u} = \sum_{ij} \int \mathbf{u} f_{ij} d\mathbf{u} = n\mathbf{v}, \tag{7}$$

$$\begin{aligned} \sum_{ij} \int \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i\right) f_{ij}^{(0)} d\mathbf{u} &= \sum_{ij} \int \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i\right) f_{ij} d\mathbf{u} \\ &= \frac{3}{2} nkT + \rho E_r + \rho E_v. \end{aligned} \tag{8}$$

Here $n = \sum_i n_i$ is the total number density, $\rho = mn$ is the mass density, ε_i is the vibrational energy of a molecule at the level i, counted from the minimum of its potential curve, E_r and E_v are, respectively, the rotational and vibrational energy per unit mass:

$$\rho E_r(T) = \sum_{ij} \int \varepsilon_j^i f_{ij} d\mathbf{u}, \qquad \rho E_v = \sum_i \varepsilon_i n_i,$$

3 Relaxation and conservation equations

The macroscopic equations associated to the Boltzmann equation (1) are obtained multiplying equation (1) by $(1, \mathbf{u}, (mc^2/2 + \varepsilon_j^i + \varepsilon_i)$, integrating over the velocity $\mathbf{u}$ and summing over rotational

levels j and over vibrational levels i (the last summation is not performed on the first equation). Under the conservative form, the macroscopic equations are written

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} + n_i \mathbf{V}_i) = R_i, \quad i = 1, ..., N, \tag{9}$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v}\mathbf{v} + \mathbf{P}) = 0, \tag{10}$$

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho \mathbf{v} E + \mathbf{P}\mathbf{v} + \mathbf{q}) = 0. \tag{11}$$

Equation (9) is the relaxation equation for the population of the ith vibrational energy level and equations (10), (11) are momentum and total energy conservation equations respectively.

The total energy per unit mass, E, is introduced as

$$\rho E = \frac{1}{2}\rho v^2 + \frac{3}{2} nkT + \rho E_r + \rho E_v,$$

the diffusion velocity $\mathbf{V}_i$ of a molecule at the ith vibrational level,

$$n_i \mathbf{V}_i = \sum_j \int \mathbf{c} f_{ij} d\mathbf{u}, \tag{12}$$

the stress tensor $\mathbf{P}$

$$\mathbf{P} = \sum_{ij} \int m \mathbf{c}\mathbf{c} f_{ij} d\mathbf{u}, \tag{13}$$

and the heat flux $\mathbf{q}$

$$\mathbf{q} = \sum_{ij} \int \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i \right) \mathbf{c} f_{ij} d\mathbf{u}. \tag{14}$$

Here $\mathbf{c}$=$\mathbf{u}$–$\mathbf{v}$ is the peculiar velocity. In the zero order approximation $\mathbf{V}_i = 0$, $\mathbf{q}$= 0, $\mathbf{P}$= $p\mathbf{I}$, p is the pressure, and $\mathbf{I}$ is the unit tensor.

The right hand side of the equation (9) is defined by

$$R_i = \sum_j \int J_{ij}^{sl} d\mathbf{u} = R_i^{vibr}. \tag{15}$$

Considering the zero order approximation, i.e. substituting f_{ij} by $f_{ij}^{(0)}$ in (15), the source term in (9) can be written as

$$R_i = R_i^{(0)} = \sum_j \int J_{ij}^{sl(0)} d\mathbf{u}. \tag{16}$$

The source term $R_i^{(0)}$ is determined by the VV and VT rate constants. Different attempts have been made to derive the VT and VV rate constants. We mention here the exact fully quantum calculations [19], the Billing closed coupled method [20], SSH theory [21], the modified FHO theory [22], [23] and also a new model using the quasi-classical multidimensional scattering theory for polyatomic gases developed by Gorbachev et al. [24], [25].

4 Chapman-Enskog's first order solution

At the first order approximation the Chapman-Enskog expansion can be written in the form:

$$f_{ij}(\mathbf{r}, \mathbf{u}, t) = f_{ij}^{(0)}(\mathbf{r}, \mathbf{u}, t)(1 + \varepsilon \phi_{ij}(\mathbf{r}, \mathbf{u}, t)), \tag{17}$$

where $f_{ij}^{(0)}$ is the zero order distribution given in the previous section. The perturbation function ϕ_{ij} is obtained solving the first order equation

$$\frac{df_{ij}^{(0)}}{dt} - J_{ij}^{sl(0)} = -\sum_k n_i n_k I_{ijk}(\phi), \tag{18}$$

where $d/dt = \partial/\partial t + \mathbf{u}.\partial/\partial \mathbf{r}$, and

$$I_{ijk}(\phi) = \frac{1}{n_i n_k} \sum_{lj'l'} \int f_{ij}^{(0)} f_{kl}^{(0)} \left(\phi_{ij} + \phi_{kl} - \phi_{ij'} - \phi_{kl'}\right) g \sigma_{ik,\,jl}^{j'l'} d^2\Omega d\mathbf{u}_1, \tag{19}$$

is the linearized collision operator of rapid processes.

The derivative $df_{ij}^{(0)}/dt$ is given by

$$\begin{aligned}
\frac{df_{ij}^{(0)}}{dt} = \; & f_{ij}^{(0)} \left\{ \left(\frac{mc^2}{2kT} - \frac{5}{2} + \mathcal{E}_{ij}^0 \right) \mathbf{c} \cdot \nabla \ln T + \right. \\
& + \frac{n}{n_i} \mathbf{c} \cdot \mathbf{d}_i + \frac{m}{kT} \left(\mathbf{cc} - \frac{1}{3} c^2 \mathbf{I} \right) : \nabla \mathbf{v} + \\
& + \left(\frac{mc^2}{3kT} - 1 - \frac{p}{\rho T (c_{tr} + c_{rot})} \left(\frac{mc^2}{2kT} - \frac{3}{2} + \mathcal{E}_{ij}^0 \right) \right) \nabla \cdot \mathbf{v} + \frac{R_i^{(0)}}{n_i} - \\
& \left. - \frac{\sum_i R_i^{(0)} \left(\frac{3}{2} kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right)}{\rho T (c_{tr} + c_{rot})} \left(\frac{mc^2}{2kT} - \frac{3}{2} + \mathcal{E}_{ij}^0 \right) \right\},
\end{aligned} \tag{20}$$

where $\mathbf{d}_i = \nabla(n_i/n)$ is the diffusion driving forces, satisfying the relation $\sum_i \mathbf{d}_i = 0$,

$$c_{tr} = \frac{3}{2} \frac{k}{m}, \qquad c_{rot} = \frac{\partial E_r}{\partial T}, \tag{21}$$

denote the translational and the rotational specific heats at constant volume (per mass unit) respectively. In Eq. (20) the following notation is introduced:

$$\mathcal{E}_{ij}^0 = \mathcal{E}_j^i - \langle \mathcal{E}_j^i \rangle_r,$$

where $\mathcal{E}_j^i = \varepsilon_j^i / kT$ and $\langle \zeta_{ij} \rangle_r$ is the averaged value of ζ_{ij} over the rotational spectrum

$$\langle \zeta_{ij} \rangle_r = \frac{\sum_j s_j^i \zeta_{ij} \exp\left(-\frac{\varepsilon_j^i}{kT} \right)}{\sum_j s_j^i \exp\left(-\frac{\varepsilon_j^i}{kT} \right)}.$$

From the expression for $df_{ij}^{(0)}/dt$, we deduce that a particular solution of equation (18) can be written as

$$\phi_{ij} = -\frac{1}{n} \mathbf{A}_{ij} \cdot \nabla \ln T - \frac{1}{n} \sum_k \mathbf{D}_{ij}^k \cdot \mathbf{d}_k - \frac{1}{n} \mathbf{B}_{ij} : \nabla \mathbf{v} - \frac{1}{n} F_{ij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{ij}. \tag{22}$$

Uniqueness of the solution is provided by adding the constraints following from the normalization conditions of the Chapman-Enskog method (6)–(8):

$$\sum_j \int f_{ij}^{(0)} \phi_{ij} d\mathbf{u} = 0, \qquad i = 1, ..., N, \tag{23}$$

$$\sum_{ij} \int f_{ij}^{(0)} \phi_{ij} \mathbf{u} d\mathbf{u} = 0, \tag{24}$$

$$\sum_{ij} \int f_{ij}^{(0)} \phi_{ij} \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i \right) d\mathbf{u} = 0. \tag{25}$$

Substituting (22) in (18) and separating the independent quantities we obtain the following integral equations

$$\sum_k \frac{n_i n_k}{n^2} I_{ijk}(\mathbf{A}) = \frac{1}{n} \left(\frac{mc^2}{2kT} - \frac{5}{2} + \mathcal{E}_{ij}^0 \right) \mathbf{c} f_{ij}^{(0)}, \tag{26}$$

$$i = 1, ..., N, \quad j = 1, ..., M,$$

$$\sum_k \frac{n_i n_k}{n^2} I_{ijk}(\mathbf{B}) = \frac{m}{nkT} \left(\mathbf{cc} - \frac{1}{3} c^2 \mathbf{I} \right) f_{ij}^{(0)}, \tag{27}$$

$$i = 1, ..., N, \quad j = 1, ..., M,$$

$$\sum_k \frac{n_i n_k}{n^2} I_{ijk}(\mathbf{D}^l) = \frac{1}{n_i} \left(\delta_{il} - \frac{n_i}{n} \right) \mathbf{c} f_{ij}^{(0)}, \tag{28}$$

$$i = 1, ..., N, \qquad l = 1, ..., N, \quad j = 1, ..., M,$$

$$\sum_k \frac{n_i n_k}{n^2} I_{ijk}(F) = \frac{1}{n} \left(\frac{mc^2}{3kT} - 1 - \frac{p}{\rho T (c_{tr} + c_{rot})} \left(\frac{mc^2}{2kT} - \frac{3}{2} + \mathcal{E}_{ij}^0 \right) \right) f_{ij}^{(0)}, \tag{29}$$

$$i = 1, ..., N, \quad j = 1, ..., M,$$

$$\begin{aligned} \sum_k \frac{n_i n_k}{n^2} I_{ijk}(G) &= -\frac{1}{n} \frac{\sum_i R_i^{(0)} \left(\frac{3}{2} kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right)}{\rho T (c_{tr} + c_{rot})} \times \\ &\times \left(\frac{mc^2}{2kT} - \frac{3}{2} + \mathcal{E}_{ij}^0 \right) f_{ij}^{(0)} - \frac{1}{n} J_{ij}^{sl(0)} + \frac{R_i^{(0)}}{n\, n_i} f_{ij}^{(0)}, \end{aligned} \tag{30}$$

$$i = 1, ..., N, \quad j = 1, ..., M,$$

where M is the total number of rotational levels. It can be shown that the form of $\mathbf{A}_{ij}$, $\mathbf{B}_{ij}$, $\mathbf{D}_{ij}^k$, F_{ij} and G_{ij} is

$$\mathbf{A}_{ij} = A_{ij}(c^2)\mathbf{c}, \tag{31}$$

$$\mathbf{B}_{ij} = B_{ij}(c^2) \left(\mathbf{cc} - \frac{1}{3} c^2 \mathbf{I} \right), \tag{32}$$

$$\mathbf{D}_{ij}^k = D_{ij}^k(c^2)\mathbf{c}, \tag{33}$$

$$F_{ij} = F_{ij}(c^2), \qquad G_{ij} = G_{ij}(c^2). \tag{34}$$

Substituting (31)-(32)-(33)-(34) in (22) and then (22) in (23)-(24)-(25), the conditions of normalization become

$$\sum_{ij} \int f_{ij}^{(0)} A_{ij} c^2 d\mathbf{u} = 0, \tag{35}$$

$$\sum_{ij} \int f_{ij}^{(0)} D_{ij}^k c^2 d\mathbf{u} = 0, \quad k = 1, ..., N, \tag{36}$$

$$\sum_{j} \int f_{ij}^{(0)} F_{ij} d\mathbf{u} = 0, \quad i = 1, ..., N, \tag{37}$$

$$\sum_{j} \int f_{ij}^{(0)} G_{ij} d\mathbf{u} = 0, \quad i = 1, ..., N, \tag{38}$$

$$\sum_{ij} \int f_{ij}^{(0)} \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i \right) F_{ij} d\mathbf{u} = 0, \tag{39}$$

$$\sum_{ij} \int f_{ij}^{(0)} \left(\frac{mc^2}{2} + \varepsilon_j^i + \varepsilon_i \right) G_{ij} d\mathbf{u} = 0. \tag{40}$$

Furthermore, as in [26], we add the relation

$$\sum_{k} \mathbf{D}_{ij}^k \frac{\rho_k}{\rho} = 0. \tag{41}$$

Now the functions $\mathbf{A}_{ij}$, $\mathbf{D}_{ij}^k$, $\mathbf{B}_{ij}$, F_{ij}, G_{ij} are uniquely determined by the corresponding integral equations and constraints (35)–(40) and (41).

To compute $\mathbf{P}$, $\mathbf{V}$ and $\mathbf{q}$, the bracket notation is used

$$[A, B] = \sum_{ijk} \frac{n_i n_k}{n^2} \int B_{ij} I_{ijk}(A) d\mathbf{u}, \tag{42}$$

which can also be written, using symmetry relations, as

$$[A, B] = \sum_{ik} \frac{n_i n_k}{n^2} \left([A, B]'_{ik} + [A, B]''_{ik} \right), \tag{43}$$

where

$$[A, B]'_{ik} = \frac{1}{2 n_i n_k} \sum_{jlj'l'} \int f_{ij}^{(0)} f_{kl}^{(0)} (B_{ij} - B_{ij'})(A_{ij} - A_{ij'}) g \sigma_{ijkl}^{j'l'} d^2\Omega d\mathbf{u}_1 d\mathbf{u}, \tag{44}$$

$$[A, B]''_{ik} = \frac{1}{2 n_i n_k} \sum_{jlj'l'} \int f_{ij}^{(0)} f_{kl}^{(0)} (B_{ij} - B_{ij'})(A_{kl} - A_{kl'}) g \sigma_{ijkl}^{j'l'} d^2\Omega d\mathbf{u}_1 d\mathbf{u}. \tag{45}$$

It follows that the stress tensor is given by

$$\mathbf{P} = (p - p_{rel})\ \mathbf{I} - 2\mu\ \mathbf{S} - \eta \nabla .\ \mathbf{v}\ \ \mathbf{I}, \tag{46}$$

where

$$p_{rel} = kT[F, G], \quad \eta = kT[F, F], \quad \mu = \frac{kT}{10}[B, B], \tag{47}$$

are the relaxation pressure, the bulk and shear viscosity coefficients respectively. The notation S denotes the tensor of deformation

$$\mathbf{S} = \left[\frac{1}{2} \left(\frac{\partial \mathbf{v}_k}{\partial \mathbf{r}_l} \right) + \left(\frac{\partial \mathbf{v}_l}{\partial \mathbf{r}_k} \right) - \frac{1}{3} \delta_{kl} \nabla . \mathbf{v} \right]_{kl}. \tag{48}$$

The diffusion velocity $\mathbf{V}_i$ is given by

$$\mathbf{V}_i = -\sum_{l} D_{il} \mathbf{d}_l - D_{Ti} \nabla log T, \tag{49}$$

where

$$D_{il} = \frac{1}{3n}[\mathbf{D}^i, \mathbf{D}^l], \tag{50}$$

$$D_{Ti} = \frac{1}{3n}[\mathbf{D}^i, \mathbf{A}]. \tag{51}$$

Here, D_{ik} and D_{Ti} are the diffusion and thermal diffusion coefficients for every vibrational species.

Finally, the heat flux $\mathbf{q}$ is given by

$$\mathbf{q} = -\lambda' \nabla T - p \sum_i D_{Ti} \mathbf{d}_i + \sum_i \left(\frac{5}{2} kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right) n_i \mathbf{V}_i, \tag{52}$$

where the coefficient of thermal conductivity, λ', is given by

$$\lambda' = \lambda_{tr} + \lambda_{rot} = \frac{k}{3}[\mathbf{A}, \mathbf{A}]. \tag{53}$$

5 Collision integrals

It is useful to introduce collision integral notations as proposed in [27]. The notations given in this section will simplify greatly transport coefficient formulas. We recall the averaging operator notation given by

$$< F >_{ik} = \left(\frac{kT}{\pi m} \right)^{1/2} \sum_{jlj'l'} \frac{s_j^i s_l^k}{Z_r^2} e^{-(\mathcal{E}_j^k + \mathcal{E}_l^k)} \int e^{-\gamma^2} F \gamma^3 \sigma_{ikjl}^{j'l'} d^2\Omega d\gamma, \tag{54}$$

where

$$\gamma = \frac{1}{2} \left(\frac{m}{kT} \right)^{1/2} g, \qquad \mathcal{E}_j^i = \frac{\varepsilon_j^i}{kT}, \tag{55}$$

are the dimensionless velocity and energy. Then, the collision integrals are defined as follows

$$\Omega_{ik}^{(1,1)} = < \gamma^2 - \gamma\gamma' cos\chi >_{ik}, \tag{56}$$

$$\Omega_{ik}^{(2,2)} = < \gamma^4 - \gamma^2\gamma'^2 cos^2\chi - \frac{1}{6}\Delta(\mathcal{E}_{ik})^2 >_{ik}, \tag{57}$$

$$\Omega_{ik}^{(1,2)} = < \gamma^4 - \gamma^3\gamma' cos\chi >_{ik}, \tag{58}$$

$$\Omega_{ik}^{(1,3)} = < \gamma^6 - \gamma^3\gamma'^3 cos\chi >_{ik}, \tag{59}$$

where

$$\Delta\mathcal{E}_{ik} = \Delta\mathcal{E}_i + \tilde{\Delta}\mathcal{E}_k, \tag{60}$$

$$\begin{cases} \Delta\mathcal{E}_i = \mathcal{E}_{j'}^i - \mathcal{E}_j^i \\ \\ \tilde{\Delta}\mathcal{E}_k = \mathcal{E}_{l'}^k - \mathcal{E}_l^k, \end{cases} \tag{61}$$

where the superscript $\tilde{}$ is used to distinguish one of the colliding partner from the other in the case i and k are the same. If $i = k$, we adopt the notation

$$\begin{cases} \tilde{\Delta}\mathcal{E}_i = \mathcal{E}_{l'}^i - \mathcal{E}_l^i \\ \\ \Delta\mathcal{E}_{ii} = \Delta\mathcal{E}_i + \tilde{\Delta}\mathcal{E}_i. \end{cases} \tag{62}$$

The following notation will also be used

$$\tilde{A}_{ik} = \frac{1}{2} \frac{\Omega_{ik}^{(2,2)}}{\Omega_{ik}^{(1,1)}}, \qquad \tilde{B}_{ik} = \frac{1}{3} \frac{5\Omega_{ik}^{(1,2)} - \Omega_{ik}^{(1,3)}}{\Omega_{ik}^{(1,1)}}, \qquad \tilde{C}_{ik} = \frac{1}{3} \frac{\Omega_{ik}^{(1,2)}}{\Omega_{ik}^{(1,1)}}. \tag{63}$$

We also introduce the binary diffusion coefficient as

$$\mathcal{D}_{ik} = \frac{3kT}{8nm}\frac{1}{\Omega_{ik}^{(1,1)}}, \tag{64}$$

and the diffusion coefficient for the rotational energy as

$$\mathcal{D}_{i\ rot,k} = \frac{3kT}{8nm}\frac{1}{\Omega_{i\ rot,k}^{(1,1)}}, \tag{65}$$

with

$$\frac{mc_{rot,i}}{k}\,\Omega_{i\ rot,i}^{(1,1)} = < \mathcal{E}_{ij}^0((\mathcal{E}_{ij}^0 - \mathcal{E}_{il}^0)\gamma^2 - (\mathcal{E}_{ij'}^0 - \mathcal{E}_{il'}^0)\gamma\gamma' cos\chi) >_{ii}, \tag{66}$$

$$\frac{mc_{rot,i}}{k}\,\Omega_{i\ rot,k}^{(1,1)} = < \mathcal{E}_{ij}^0(\mathcal{E}_{ij}^0\gamma^2 - \mathcal{E}_{ij'}^0\gamma\gamma' cos\chi) >_{ik}, \quad (i \neq k), \tag{67}$$

where

$$\mathcal{E}_{ij}^0 = \mathcal{E}_j^i - < \mathcal{E}_j^i >_r . \tag{68}$$

In formulas (66) and (67), the partial specific heats per mass unit, $c_{rot,i}$, is defined by

$$c_{rot,i} = \frac{\partial E_r^i}{\partial T}, \tag{69}$$

where the rotational energy for particles in vibrational level i is given by

$$E_r^i = \frac{1}{\rho_i}\sum_j \int \varepsilon_j^i f_{ij} d\ \mathbf{u}. \tag{70}$$

Furthermore, the following relations hold

$$E_r = \sum_i \frac{n_i}{n} E_r^i, \qquad c_{rot} = \sum_i \frac{n_i}{n} c_{rot,i}, \tag{71}$$

$$c_{rot,i} = \frac{k}{m}\Big(< (\mathcal{E}_j^i)^2 >_r - (< \mathcal{E}_j^i >_r)^2 \Big). \tag{72}$$

6 Approximations of the transport coefficients

In order to derive the transport coefficients, it is needed to determine the unknowns $\mathbf{A}_{ij}$, $\mathbf{B}_{ij}$, $\mathbf{D}_{ij}^l$ and F_{ij}. As proved numerically by [28], [4], the relaxation pressure is small compared to nkT and may be neglected. The previous unknowns are classically approximated by polynomials expansions: Laguerre and Sonine for translational energy and Wang Chang and Uhlenbeck polynomials for rotational energy [1].

Laguerre and Sonine polynomials are given by the following formula

$$S_l^{(n)}(x) = \sum_{p=0}^{n} \frac{(l+n)!}{(l+n)!p!(n-p)!}(-x)^p, \tag{73}$$

and satisfy the orthogonality property

$$\int x^l e^{-x} S_l^{(n)}(x) S_l^{(p)}(x) dx = \begin{cases} 0 \text{ if } n \neq p \\ \dfrac{(l+n)!}{n!} \text{ if } n = p. \end{cases} \tag{74}$$

In the previous formula, we use the convention that

$$\left(\frac{l}{2}\right)! = \frac{l}{2} \times \frac{l-1}{2} \times .... \times \frac{1}{2}\sqrt{\pi}.$$

The first polynomials are $S_l^{(0)}(x) = 1$, $S_l^{(1)}(x) = (l+1) - x$.

The Wang Chang and Uhlenbeck polynomials, for the discrete case, are written as

$$W^{(p)}(y) = -yW^{(p-1)}(y) + \sum_{q=0}^{p-1} \frac{\langle yW^{(p-1)}(y)W^{(q)}(y)\rangle_r}{\langle W^{(q)2}\rangle_r} W^{(q)}(y). \tag{75}$$

where the first polynomials are $W^{(0)} = 1$, $W^{(1)} = \langle y\rangle_r - y$. It is easy to check the following orthogonality property

$$\langle W^{(p)}W^{(r)}\rangle_r = 0 \quad \text{if } p \neq r. \tag{76}$$

Thus, the expressions of $\mathbf{A}_{ij}$, $\mathbf{B}_{ij}$, $\mathbf{D}_{ij}^l$, F_{ij} are

$$\mathbf{A}_{ij} = -\left(\frac{m}{2kT}\right)^{1/2} \mathcal{C} \sum_{r,p=0}^{\infty} a_{rp}^i S_{3/2}^{(r)}(\mathcal{C}^2) W^{(p)}(\mathcal{E}_j^i), \tag{77}$$

$$\mathbf{B}_{ij} = \left(\mathcal{C}\mathcal{C} - \frac{1}{3}\mathcal{C}^2\mathbf{I}\right) \sum_{r=0}^{\infty} b_r^i S_{5/2}^{(r)}(\mathcal{C}^2), \tag{78}$$

$$\mathbf{D}_{ij}^l = \left(\frac{m}{2kT}\right)^{1/2} \mathcal{C} \sum_{r,p=0}^{\infty} d_{rp}^{l,i} S_{3/2}^{(r)}(\mathcal{C}^2) W^{(p)}(\mathcal{E}_j^i), \tag{79}$$

$$\mathrm{F}_{ij} = \sum_{r,p=0}^{\infty} f_{rp}^i S_{1/2}^{(r)}(\mathcal{C}^2) W^{(p)}(\mathcal{E}_j^i), \tag{80}$$

where $\mathcal{C} = (m/2kT)^{1/2}c$. The values $l = 1/2, 3/2, 5/2$ are chosen for later convenience.

Substituting (77)-(80) in (35)-(40), the conditions of normalization become

$$\sum_i \frac{n_i}{n} a_{00}^i = 0, \tag{81}$$

$$\sum_i \frac{n_i}{n} d_{0,0}^{k,i} = 0, \qquad k = 1, ..., N, \tag{82}$$

$$f_{00}^i = 0, \qquad i = 1, ..., N,$$

$$\sum_i \frac{n_i}{n}(c_{tr} f_{10}^i + c_{rot,i} f_{01}^i) = 0. \tag{83}$$

After some algebra, the transport coefficients are written as

$$D_{Ti} = \frac{1}{3n}[\mathbf{D}^i, \mathbf{A}] = -\frac{1}{2n} a_{00}^i, \tag{84}$$

$$D_{il} = \frac{1}{3n}[\mathbf{D}^i, \mathbf{D}^l] = \frac{1}{2n} d_{0,0}^{l,i}, \tag{85}$$

$$\lambda' = \lambda_{tr} + \lambda_{rot} = \frac{k}{3}[\mathbf{A}, \mathbf{A}] = \frac{5}{4}k \sum_i \frac{n_i}{n} a_{10}^i + \frac{1}{2}m \sum_i \frac{n_i}{n} c_{rot,i} a_{01}^i, \tag{86}$$

$$\mu = \frac{kT}{10}[B,B] = \frac{kT}{2}\sum_i \frac{n_i}{n} b_0^i, \tag{87}$$

$$\begin{aligned} \eta &= kT[F,F] = \frac{kT}{c_{tr}+c_{rot}}\sum_i \frac{n_i}{n}(-c_{rot}f_{10}^i + c_{rot,i}f_{01}^i) \\ &= \frac{kT}{c_{tr}}\sum_i \frac{n_i}{n} c_{rot,i} f_{01}^i = -kT\sum_i \frac{n_i}{n} f_{10}^i. \end{aligned} \tag{88}$$

7 Computation of the transport coefficients

In this section, we calculate the coefficients a_{rp}^i, b_r^i, $d_{rp}^{l,i}$ and f_{rp}^i of the polynomials expansions given in the previous section. They are solutions of algebraic systems obtained multiplying equations (26), (27), (27) and (27) by an appropriate Laguerre-Sonine and Wang Chang-Uhlenbeck polynomial, integrating over the velocity, and summing over rotational quantum level j. Systems, similar to those given in this section, were calculated in [18], [29], in the case of polyatomic gas mixtures with internal energy, and in the case of independent energy modes [30].

The general system associated to the coefficients $a_{r'p'}^i$ is written

$$\left\{ \begin{array}{c} \displaystyle\sum_k \sum_{r'p'} \Lambda_{r'p'rp}^{ik} a_{r'p'}^k = \frac{15}{2}\frac{n_i}{n} kT\delta_{r1}\delta_{p0} + 3\frac{n_i}{n} mTc_{rot,i}\delta_{r0}\delta_{p1}, \\ r,p = 0,1,...,\ i = 1,...,N, \end{array} \right. \tag{89}$$

where

$$\Lambda_{r'p'rp}^{ik} = m\left(\sum_h \frac{n_i n_h}{n^2}[SW^{(r'p')}, SW^{(rp)}]'_{ih}\delta_{ik} + \frac{n_i n_k}{n^2}[SW^{(r'p')}, SW^{(rp)}]''_{ik} \right), \tag{90}$$

$$SW^{(rp)} = \mathcal{C}S_{3/2}^{(r)}(\mathcal{C}^2)W^{(p)}(\mathcal{E}_j^i). \tag{91}$$

From the definition of the bracket integrals, the following property holds

$$\Lambda_{r'p'rp}^{ik} = \Lambda_{rpr'p'}^{ki}. \tag{92}$$

Furthermore, it results from the momentum conservation in a collision that system (89) is not linearly independent for $p = r = 0$. In this case system (89) is completed by the constraint

$$\sum_i \frac{n_i}{n} a_{00}^i = 0. \tag{93}$$

Keeping the first non-vanishing coefficients of the expansions we obtain the following system

$$\left\{ \begin{array}{l} \displaystyle\sum_k (\Lambda_{0000}^{ik}a_{00}^k + \Lambda_{1000}^{ik}a_{10}^k + \Lambda_{0100}^{ik}a_{01}^k) = 0, \quad i = 1,...,N, \\ \displaystyle\sum_k (\Lambda_{0010}^{ik}a_{00}^k + \Lambda_{1010}^{ik}a_{10}^k + \Lambda_{0110}^{ik}a_{01}^k) = \frac{15}{2}\frac{n_i}{n}kT, \quad i = 1,...,N, \\ \displaystyle\sum_k (\Lambda_{0001}^{ik}a_{00}^k + \Lambda_{1001}^{ik}a_{10}^k + \Lambda_{0101}^{ik}a_{01}^k) = 3\frac{n_i}{n}mTc_{rot,i}, \quad i = 1,...,N. \end{array} \right. \tag{94}$$

After some calculation, the coefficients of system (94) are written as

$$\Lambda_{0000}^{ik} = -\frac{3kT}{2n}\frac{x_i x_k}{\mathcal{D}_{ik}}, \qquad (i \neq k), \tag{95}$$

$$\Lambda_{0000}^{ii} = \frac{3kT}{2n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}, \tag{96}$$

$$\Lambda^{ik}_{1000} = \frac{3kT}{8n}\frac{x_i x_k}{\mathcal{D}_{ik}}(6\tilde{C}_{ik} - 5), \qquad (i \neq k), \tag{97}$$

$$\Lambda^{ii}_{1000} = -\frac{3kT}{8n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}(6\tilde{C}_{ih} - 5), \tag{98}$$

$$\Lambda^{ik}_{0100} = \frac{3kT}{2n}x_i x_k \frac{< \mathcal{E}^0_{kl}(\gamma^2 - \gamma\gamma' cos\chi) >_{ik}}{\Omega^{(1,1)}_{ik}\mathcal{D}_{ik}}, \qquad (i \neq k), \tag{99}$$

$$\Lambda^{ii}_{0100} = -\frac{3kT}{2n}\sum_{h\neq i} x_i x_h \frac{< \mathcal{E}^0_{ij}(\gamma^2 - \gamma\gamma' cos\chi) >_{ih}}{\Omega^{(1,1)}_{ih}\mathcal{D}_{ih}}, \tag{100}$$

$$\Lambda^{ik}_{1010} = -\frac{3kT}{8n}\frac{x_i x_k}{\mathcal{D}_{ik}}\left(\frac{55}{4} - 3\tilde{B}_{ik} - 4\tilde{A}_{ik} - \frac{25}{12}\frac{< (\Delta\mathcal{E}_{ik})^2 >_{ik}}{\Omega^{(1,1)}_{ik}}\right), \qquad (i \neq k), \tag{101}$$

$$\begin{aligned}\Lambda^{ii}_{1010} &= \frac{3kT}{8n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}\left(\frac{55}{4} - 3\tilde{B}_{ih} + 4\tilde{A}_{ih} + \frac{25}{12}\frac{< (\Delta\mathcal{E}_{ih})^2 >_{ih}}{\Omega^{(1,1)}_{ih}}\right) + \\ &+ \frac{3kT}{4n}\frac{x_i^2}{\mathcal{D}_{ii}}\left(4\tilde{A}_{ii} + \frac{25}{12}\frac{< (\Delta\mathcal{E}_{ii})^2 >_{ii}}{\Omega^{(1,1)}_{ii}}\right),\end{aligned} \tag{102}$$

$$\begin{aligned}\Lambda^{ik}_{0110} &= -\frac{3kT}{4n}\frac{x_i x_k}{\mathcal{D}_{ik}}\left[\frac{5}{4}\frac{< \tilde{\Delta}\mathcal{E}_k \Delta\mathcal{E}_{ik} >_{ik}}{\Omega^{(1,1)}_{ik}} - \frac{5}{2}\frac{< \mathcal{E}^0_{kl}(\gamma^2 - \gamma\gamma' cos\chi) >_{ik}}{\Omega^{(1,1)}_{ik}}\right. \\ &\left. + \frac{< \mathcal{E}^0_{kl}(\gamma^4 - \gamma\gamma'^3 cos\chi) >_{ik}}{\Omega^{(1,1)}_{ik}}\right], \qquad (i \neq k),\end{aligned} \tag{103}$$

$$\begin{aligned}\Lambda^{ii}_{0110} &= -\frac{3kT}{4n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}\left[\frac{5}{4}\frac{< \Delta\mathcal{E}_i \Delta\mathcal{E}_{ih} >_{ih}}{\Omega^{(1,1)}_{ih}} + \frac{5}{2}\frac{< \mathcal{E}^0_{ij}(\gamma^2 - \gamma\gamma' cos\chi) >_{ih}}{\Omega^{(1,1)}_{ih}}\right. \\ &\left. - \frac{< \mathcal{E}^0_{ij}(\gamma^4 - \gamma\gamma'^3 cos\chi) >_{ih}}{\Omega^{(1,1)}_{ih}}\right] - \frac{15kT}{16n}\frac{x_i^2}{\mathcal{D}_{ii}}\frac{< (\Delta\mathcal{E}_{ii})^2 >_{ii}}{\Omega^{(1,1)}_{ii}},\end{aligned} \tag{104}$$

$$\Lambda^{ik}_{0101} = -\frac{3kT}{2n}\frac{x_i x_k}{\mathcal{D}_{ik}}\left[\frac{< \mathcal{E}^0_{ij}(\mathcal{E}^0_{kl}\gamma^2 - \mathcal{E}^0_{kl'}\gamma\gamma' cos\chi) >_{ik}}{\Omega^{(1,1)}_{ik}} - \frac{3}{4}\frac{< \Delta\mathcal{E}_i \tilde{\Delta}\mathcal{E}_k >_{ik}}{\Omega^{(1,1)}_{ik}}\right], \qquad (i \neq k), \tag{105}$$

$$\begin{aligned}\Lambda^{ii}_{0101} &= \frac{3kT}{2n}\sum_{h\neq i} x_i x_h\left[\frac{mc_{rot,i}}{k\mathcal{D}_{i\ rot,h}} + \frac{3}{4}\frac{< (\Delta\mathcal{E}_i)^2 >_{ih}}{\Omega^{(1,1)}_{ih}\mathcal{D}_{ih}}\right] + \\ &+ \frac{3kT}{2n}x_i^2\left[\frac{mc_{rot,i}}{k\mathcal{D}_{i\ rot,i}} + \frac{3}{8}\frac{< (\Delta\mathcal{E}_{ii})^2 >_{ii}}{\Omega^{(1,1)}_{ii}\mathcal{D}_{ii}}\right].\end{aligned} \tag{106}$$

The system associated to the coefficients $b^k_{r'}$ is written as

$$\begin{cases} \displaystyle\sum_k\sum_{r'} H^{ik}_{r'r} b^k_{r'} = 5\frac{n_i}{n}\delta_{r0}, \\ \\ r = 0, 1, ..., \quad i = 1, .., N, \end{cases} \tag{107}$$

where

$$H^{ik}_{r'r} = \sum_h \frac{n_i n_h}{n^2}[SW^{(r')}, SW^{(r)}]'_{ih}\delta_{ik} + \frac{n_i n_k}{n^2}[SW^{(r')}, SW^{(r)}]''_{ik}, \tag{108}$$

$$SW^{(r)} = \left(\mathcal{C}\mathcal{C} - \frac{\mathcal{C}^2}{3}\right) S^{(r)}_{5/2}(\mathcal{C}^2). \tag{109}$$

Considering the first non-vanishing coefficients, the general system reduces to

$$\sum_k H^{ik}_{00} b^k_0 = 5\frac{n_i}{n}, \qquad i = 1, .., N, \tag{110}$$

where

$$\begin{cases} H^{ik}_{00} = 2x_i x_k \left[-\dfrac{10}{3}\Omega^{(1,1)}_{ik} + \Omega^{(2,2)}_{ik}\right], \qquad (i \neq k) \\ \\ H^{ii}_{00} = 2\displaystyle\sum_{h\neq i} x_i x_h \left[\frac{10}{3}\Omega^{(1,1)}_{ih} + \Omega^{(2,2)}_{ih}\right] + 4x_i^2\Omega^{(2,2)}_{ii}. \end{cases} \tag{111}$$

The system associated to the coefficients $d^{l,k}_{r'p'}$ is written as

$$\begin{cases} \displaystyle\sum_k \sum_{r'p'} \gamma^{ik}_{r'r} d^{l,k}_{r'p'} = 3kT\left(\delta_{il} - \frac{n_i}{n}\right)\delta_{r0}\delta_{p0}, \\ r, p = 0, 1, ..., \quad i, l = 1, ..., N, \end{cases} \tag{112}$$

where

$$\gamma^{ik}_{r'p'rp} = m\left(\sum_h \frac{n_i n_h}{n^2}[SW^{(r'p')}, SW^{(rp)}]'_{ih}\delta_{ik} + \frac{n_i n_k}{n^2}[SW^{(r'p')}, SW^{(rp)}]''_{ik}\right), \tag{113}$$

$$SW^{(rp)} = \mathcal{C}S^{(r)}_{3/2}(\mathcal{C}^2)W^{(p)}(\mathcal{E}^i_j). \tag{114}$$

It is obvious that $\gamma^{ik}_{r'p'rp} = \Lambda^{ik}_{r'p'rp}$. Though it is possible to consider only the coefficients $d^{l,k}_{00}$, we may consider coefficients $d^{l,k}_{rp}$ for $(r,p) = (0,0), (1,1), (0,1)$. The resulting system can be deduced from (94), substituting in each equation, the right hand side by

$$3kT\left(\delta_{il} - \frac{n_i}{n}\right), \qquad 0, \qquad 0,$$

respectively.

Finally, the general system associated to the coefficients f^i_{rp} is given by

$$\begin{cases} \displaystyle\sum_k \sum_{r'p'} I^{ik}_{r'p'rp} f^k_{r'p'} = \frac{n_i}{n}\frac{1}{c_{tr} + c_{rot}}(-c_{rot}\delta_{p0}\delta_{r1} + c_{rot,i}\delta_{p1}\delta_{r0}), \\ \\ \qquad\qquad r, p = 1, ..., \quad i = 1, ..., N, \end{cases} \tag{115}$$

where

$$I^{ik}_{r'p'rp} = \left(\sum_h \frac{n_i n_h}{n^2}[SW^{(r'p')}, SW^{(rp)}]'_{ih}\delta_{ik} + \frac{n_i n_k}{n^2}[SW^{(r'p')}, SW^{(rp)}]''_{ik}\right), \tag{116}$$

$$SW^{(rp)} = S^{(r)}_{1/2}(\mathcal{C}^2)W^{(p)}(\mathcal{E}^i_j). \tag{117}$$

From the definition of the bracket integral, the following property holds

$$I^{ik}_{r'p'rp} = I^{ki}_{rpr'p'}. \tag{118}$$

Furthermore, for $r = p = 0$, system (115) is not linearly independent. This is a consequence of the total energy conservation in a collision. In that case, system (115) is supplemented by the constraint equation

$$\sum_i \frac{n_i}{n}(c_{tr} f^i_{10} + c_{rot,i} f^i_{01}) = 0. \tag{119}$$

In practice, system (115) is solved for $(r,p) = (1,0),(0,1)$, ie. only the first nonvanishing coefficients in the expansion (80) are considered. With the previous hypothesis, we write

$$\left\{ \begin{array}{l} \displaystyle\sum_k (I^{ik}_{1010} f^k_{10} + I^{ik}_{0110} f^k_{01}) = -\frac{n_i}{n} \frac{c_{rot}}{c_{tr}+c_{rot}}, \quad i = 1,...,N, \\ \\ \displaystyle\sum_k (I^{ik}_{1001} f^k_{10} + I^{ik}_{0101} f^k_{01}) = \frac{n_i}{n} \frac{c_{rot,i}}{c_{tr}+c_{rot}}, \quad i = 1,...,N. \end{array} \right. \tag{120}$$

After simple algebra, coefficients of system (120) may be expressed as

$$I^{ik}_{1010} = x_i x_k \left[-4\Omega^{(1,1)}_{ik} + < (\Delta\mathcal{E}_{ik})^2 >_{ik} \right], \qquad (i \neq k), \tag{121}$$

$$I^{ii}_{1010} = \sum_{h \neq i} x_i x_h \left[4\Omega^{(11)}_{ih} + < (\Delta\mathcal{E}_{ih})^2 >_{ih} \right] + 2x_i^2 < (\Delta\mathcal{E}_{ii})^2 >_{ii}, \tag{122}$$

$$I^{ik}_{0110} = -2x_i x_k < (\tilde{\Delta}\mathcal{E}_k)\,(\Delta\mathcal{E}_{ik}) >_{ik}, \qquad (i \neq k), \tag{123}$$

$$I^{ii}_{0110} = -2 \sum_{h \neq i} x_i x_h < (\Delta\mathcal{E}_{ih})\,(\Delta\mathcal{E}_i) >_{ih} -2x_i^2 < (\Delta\mathcal{E}_{ii})^2 >_{ii}, \tag{124}$$

$$I^{ik}_{0101} = 4x_i x_k < (\Delta\mathcal{E}_i)\,(\tilde{\Delta}\mathcal{E}_k) >_{ik}, \qquad (i \neq k), \tag{125}$$

$$I^{ii}_{0101} = 4 \sum_{h \neq i} x_i x_h < (\Delta\mathcal{E}_i)^2 >_{ih} +2x_i^2 < (\Delta\mathcal{E}_i)^2 >_{ii} . \tag{126}$$

We point out that only new definitions have been introduced to express the coefficients of the different systems, no approximation has been made at this level.

8 Approximations and Relaxation times

In this section, we define relaxation times, as done by [31], assuming that molecules in the different vibrational levels are molecules of different species. Moreover, taking into account additional physical approximations, used by [31], we give simplified expressions for the systems given in the previous section.

Considering that only the term associated to F_{ij} remains different from zero in the Chapman-Enskog distribution [31], [17], we write

$$f_{ij} = f^{(0)}_{ij}(T)(\mathbf{r},\mathbf{u},t) \left(1 - \frac{1}{n} S^{(1)}_{1/2}(\mathcal{C}^2) f^i_{10} \nabla\cdot\mathbf{v} - \frac{1}{n} W^{(p)}(\mathcal{E}^i_j) f^i_{01} \nabla\cdot\mathbf{v}) \right). \tag{127}$$

Then, if we linearize the Maxwellian-Boltzmann distribution

$$f^{t,r}_{ij} = \left(\frac{m}{2\pi k T_{tr}} \right)^{3/2} \frac{n_i}{Z^r_i(T^i_r)} s^i_j exp \left(-\frac{m}{2kT_{tr}} (\mathbf{u}-\mathbf{v})^2 - \frac{\varepsilon^i_j}{kT^i_r} \right), \tag{128}$$

with different translational , T_{tr}, and rotational T^i_r, temperatures, and if we indentify the resulting espressions with (127), we may write

$$\left\{ \begin{array}{l} \displaystyle\frac{(T_{tr}-T)}{T} = f^i_{10} \frac{\nabla v}{n}, \\ \\ \displaystyle\frac{(T^i_r - T)}{T} = f^i_{01} \frac{\nabla v}{n}. \end{array} \right. \tag{129}$$

After some algebra, the relaxation equation for E_r^i is written as

$$\frac{dE_r^i}{dt} = -\sum_k x_k \frac{4kn}{m} < (\Delta\mathcal{E}_i)^2 >_{ik} \left[T_r^i - T_{tr}\right]. \tag{130}$$

To derive (130), we have made the approximation that complex collisions are rare. Complex collisions are those involving more than a single quantum jump. In particular, we have the relation $\Delta\mathcal{E}_i\Delta\mathcal{E}_k = 0$ for $i \neq k$. Furthermore, we have assumed that vibrational relaxation is very slow and does not affect the rotational relaxation.

The energy E_r^i is defined by the relation

$$E_r^i = \frac{1}{\rho_i}\sum_j \int \varepsilon_j^i f_{ij}^{(0)}(1+\phi_{ij})d\mathbf{u}. \tag{131}$$

The corresponding quantity evaluated with an equilibrium distribution function for an arbitrary temperature T_0 is

$$E_r^{i(0)}(T_0) = \frac{1}{\rho_i}\sum_j \int \varepsilon_j^i f_{ij}^{(0)} d\mathbf{u}. \tag{132}$$

It follows that equation (130) may be written

$$\frac{dE_r^i}{dt} = -\frac{1}{\tau_i}\left[E_r^i - E_r^{i(0)}\right], \tag{133}$$

where the relaxation time τ_i, for the ith vibrational level, is given by

$$\frac{1}{\tau_i} = \sum_k \frac{x_k}{\tau_{ik}}, \tag{134}$$

where

$$\frac{1}{\tau_{ik}} = \frac{4kn}{mc_{rot,i}} < (\Delta\mathcal{E}_i)^2 >_{ik}, \tag{135}$$

is the cross relaxation time. Following Mason et al. [31], we introduce a collision number, related to the cross relaxation time, by the relation

$$\zeta_{ik} = \frac{4}{\pi}\frac{p\tau_{ik}}{\eta_{ik}}, \tag{136}$$

with η_{ik} a fictitious viscosity defined as

$$\eta_{ik} = \frac{5}{8}\frac{kT}{\Omega_{ik}^{(2,2)}}. \tag{137}$$

In practice, η_{ik} may be determined by

$$\frac{\rho}{2}\mathcal{D}_{ik} = \frac{3}{5}\tilde{A_{ik}}\eta_{ik}. \tag{138}$$

We also have, under the approximation of rare complex collisions, the following relations

$$< (\Delta\mathcal{E}_{ii})^2 >_{ii} = \frac{2mTc_{rot,i}}{\pi\eta_{ii}}\frac{1}{\zeta_{ii}}, \tag{139}$$

and

$$< \Delta\mathcal{E}_i\Delta\mathcal{E}_{ik} >_{ik} = \frac{mTc_{rot,i}}{\pi\eta_{ik}}\frac{1}{\zeta_{ik}}. \tag{140}$$

Assuming that the internal and translation motion are uncorrelated, the following equalities hold

$$< \mathcal{E}^0_{ij}\gamma^r(\gamma^s - \gamma'^s cos\chi) >_{ik} = 0, \qquad r,s \geq 0, \tag{141}$$

$$< \mathcal{E}^0_{ij}\gamma^r(\mathcal{E}^0_{kl}\gamma^s - \mathcal{E}^0_{kl'}\gamma'^s cos\chi) >_{ik} = 0, \qquad (i \neq k). \tag{142}$$

With the previous approximations, the matrix I may be written

$$\begin{aligned}
I^{ik}_{1010} &= -\frac{5}{4}kT\frac{x_i x_k}{\tilde{A}_{ik}\eta_{ik}} + \frac{T}{\pi}\frac{x_i x_k}{\eta_{ik}}\left(\frac{mc_{rot,i}}{\zeta_i} + \frac{mc_{rot,k}}{\zeta_k}\right), \qquad (i \neq k),\\
I^{ii}_{1010} &= kT\sum_{h\neq i}\left[\frac{5}{4}\frac{x_i x_h}{\tilde{A}_{ih}\eta_{ih}} + \frac{1}{k\pi}\frac{x_i x_h}{\eta_{ih}}\left(\frac{mc_{rot,i}}{\zeta_i} + \frac{mc_{rot,h}}{\zeta_h}\right)\right] + \frac{4T}{\pi}\frac{x_i^2}{\eta_{ii}}\frac{mc_{rot,i}}{\zeta_i},\\
I^{ik}_{0110} &= -\frac{2T}{\pi}\frac{x_i x_k}{\eta_{ik}}\frac{mc_{rot,k}}{\zeta_k}, \qquad (i \neq k),\\
I^{ii}_{0110} &= -\frac{2T}{\pi}\sum_{h\neq i}\frac{x_i x_h}{\eta_{ih}}\frac{mc_{rot,i}}{\zeta_i} - \frac{4T}{\pi}\frac{x_i^2}{\eta_{ii}}\frac{mc_{rot,i}}{\zeta_i},\\
I^{ik}_{0101} &= 0, \qquad (i \neq k),\\
I^{ii}_{0101} &= \frac{4T}{\pi}\sum_{h\neq i}\frac{x_i x_h}{\eta_{ih}}\frac{mc_{rot,i}}{\zeta_i} + \frac{4T}{\pi}\frac{x_i^2}{\eta_{ii}}\frac{mc_{rot,i}}{\zeta_i},
\end{aligned} \tag{143}$$

the matrix Λ may be written

$$\Lambda^{ik}_{0000} = -\frac{3kT}{2n}\frac{x_i x_k}{\mathcal{D}_{ik}}, \qquad (i \neq k), \tag{144}$$

$$\Lambda^{ii}_{0000} = \frac{3kT}{2n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}, \tag{145}$$

$$\Lambda^{ik}_{1000} = \frac{3kT}{8n}\frac{x_i x_k}{\mathcal{D}_{ik}}(6\tilde{C}_{ik} - 5), \qquad (i \neq k), \tag{146}$$

$$\Lambda^{ii}_{1000} = -\frac{3kT}{8n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}(6\tilde{C}_{ih} - 5), \tag{147}$$

$$\Lambda^{ik}_{0100} = 0, \tag{148}$$

$$\Lambda^{ik}_{1010} = -\frac{3kT}{8n}\frac{x_i x_k}{\mathcal{D}_{ik}}\left[\frac{55}{4} - 3\tilde{B}_{ik} - 4\tilde{A}_{ik} - \frac{20}{3}\frac{\tilde{A}_{ik}}{k\pi}\left(\frac{mc_{rot,i}}{\zeta_i} + \frac{mc_{rot,k}}{\zeta_k}\right)\right], \qquad (i \neq k), \tag{149}$$

$$\begin{aligned}
\Lambda^{ii}_{1010} \;=\; & \frac{3kT}{8n}\sum_{h\neq i}\frac{x_i x_h}{\mathcal{D}_{ih}}\left[\frac{55}{4} - 3\tilde{B}_{ih} + 4\tilde{A}_{ih} + \frac{20}{3}\frac{\tilde{A}_{ih}}{k\pi}\left(\frac{mc_{rot,i}}{\zeta_i} + \frac{mc_{rot,h}}{\zeta_h}\right)\right] +\\
& + \frac{3kT}{2n}\frac{x_i^2}{\mathcal{D}_{ii}}\left[2\tilde{A}_{ii} + \frac{20}{3}\frac{\tilde{A}_{ii}}{k\pi}\frac{mc_{rot,i}}{\zeta_i}\right],
\end{aligned} \tag{150}$$

$$\Lambda^{ik}_{0110} = -\frac{3T}{n\pi}\tilde{A}_{ik}\frac{x_i x_k}{\mathcal{D}_{ik}}\frac{mc_{rot,k}}{\zeta_k}, \qquad (i \neq k), \tag{151}$$

$$\Lambda^{ii}_{0110} = -\frac{3T}{n\pi}\sum_{h\neq i}\tilde{A}_{ih}\frac{x_i x_h}{\mathcal{D}_{ih}}\frac{mc_{rot,i}}{\zeta_i} - \frac{6T}{n\pi}\tilde{A}_{ii}\frac{x_i^2}{\mathcal{D}_{ii}}\frac{mc_{rot,i}}{\zeta_i}, \tag{152}$$

$$\Lambda^{ik}_{0101} = 0, \qquad (i \neq k), \tag{153}$$

$$\begin{aligned}\Lambda^{ii}_{0101} &= \frac{3T}{2n}\sum_{h\neq i}x_i x_h\frac{mc_{rot,i}}{\mathcal{D}_{i\,rot,h}} + \frac{3T}{2n}x_i^2\frac{mc_{rot,i}}{\mathcal{D}_{i\,rot,i}} + \\ &+\frac{18T}{5n\pi}\sum_{h\neq i}\tilde{A}_{ih}\frac{x_i x_h}{\mathcal{D}_{ih}}\frac{mc_{rot,i}}{\zeta_i} + \frac{18T}{5n\pi}\tilde{A}_{ii}\frac{x_i^2}{\mathcal{D}_{ii}}\frac{mc_{rot,i}}{\zeta_i},\end{aligned} \tag{154}$$

and the matrix H may be written

$$H^{ik}_{00} = \frac{5}{4}kT\frac{x_i x_k}{\eta_{ik}}\left[-\frac{5}{3\tilde{A}_{ik}}+1\right], \qquad (i \neq k), \tag{155}$$

$$H^{ii}_{00} = \frac{5}{4}kT\sum_{h\neq i}\frac{x_i x_h}{\eta_{ih}}\left[\frac{5}{3\tilde{A}_{ih}}+1\right] + \frac{5}{2}kT\frac{x_i^2}{\eta_{ii}}. \tag{156}$$

In deriving these new coefficients, the following approximation was asumed: ζ_{ik} is approximated by $\zeta_{ii} = \zeta_i$.

At this level it is quite impossible to compute the coefficients of the previous systems due to the complexity of the collision integrals. Numerical values of collision integrals are not available in the literature in the general case.

Before endding this section, we want to introduce the approximations commonly used in practice. They are

(1) Approximation of rotational diffusion coefficients $\mathcal{D}_{i\,rot,k}$ by ordinary diffusion coefficients $\mathcal{D}_{ik}$,

(2) approximation of collision integrals $\Omega^{(r,s)}_{ik}$ (and thus $\tilde{A}_{ik}$, $\tilde{B}_{ik}$, $\tilde{C}_{ik}$) by calculated elastic values.

Furthermore, the collision integrals $\Omega^{(r,s)}_{ik}$ are normalized by the corresponding value, noted $[\Omega^{(r,s)}_{ik}]_{RS}$, computed for the rigid sphere model and given by

$$[\Omega^{(r,s)}_{ik}]_{RS} = \left(\frac{kT}{m\pi}\right)^{1/2}\frac{(s+1)!}{2}\left[1-\frac{1+(-1)^r}{2(r+1)}\right]\pi\sigma_{ik}^2, \tag{157}$$

where $\sigma_{ik} = \frac{1}{2}(\sigma_i + \sigma_k)$ is the separation of the center of the two molecules, whose diameters are σ_i and σ_k respectively. Thus, we may write

$$\Omega^{(r,s)*}_{ik} = \frac{\Omega^{(r,s)}_{ik}}{[\Omega^{(r,s)}_{ik}]_{RS}} \tag{158}$$

We can now rewrite the fictious viscosity η_{ik} and the diffusion coefficients $\mathcal{D}_{ik}$, using approximation (2),

$$\eta_{ik} = \frac{5}{16}\frac{(\pi mkT)^{1/2}}{\pi\sigma_{ik}^2\,\Omega^{(2,2)*}_{ik}}, \tag{159}$$

$$\mathcal{D}_{ik} = \frac{3}{8nm}\frac{(\pi mkT)^{1/2}}{\pi\sigma_{ik}^2\,\Omega^{(1,1)*}_{ik}}. \tag{160}$$

The integrals $\Omega_{ik}^{(r,s)}$ have been calculated by many authors, for more or less complex potentiels. The dependence upon the vibrational energy levels appears through constants attached to the molecule under consideration; for example, the molecular diameter and the minimum potentiel for the Lennard-Jones potentiel. Assuming that these constants do not depend on the vibrational energy levels, it follows that the quantities $\Omega_{ik}^{(r,s)}$ do not depend on the vibrational energy levels either. Thus we can write $\Omega_{ik}^{(r,s)} = \Omega^{(r,s)}$.

As a result, the shear viscosity may be calculated directely, and after some algebra, we obtain

$$\mu = \frac{5}{16} \frac{(\pi m k T)^{1/2}}{\pi \sigma^2 \, \Omega^{(2,2)*}}. \tag{161}$$

Furthermore, assuming constant specific heat $c_{rot,i} = c_{rot}$ and constant collision number $\zeta_i = \zeta$, the bulk viscosity is given by

$$\eta = \frac{k\pi}{4m} \frac{c_{rot}}{(c_{rot} + c_{tr})^2} \zeta \eta', \tag{162}$$

where η' is given by formula (159) with no dependence on vibrational levels. Under the same hypothesis, the thermal conductivity is given by

$$\lambda' = \frac{5}{4} k A_{10} + \frac{1}{2} m c_{rot} A_{01}, \tag{163}$$

where A_{10} and A_{01} are solution of the following system

$$\begin{cases} \dfrac{3}{4n\mathcal{D}} \left(4\tilde{A} + \dfrac{40\tilde{A} m c_{rot}}{3k\pi\zeta} \right) A_{10} - \dfrac{6\tilde{A} m c_{rot}}{kn\pi\mathcal{D}\zeta} A_{01} = \dfrac{15}{2}, \\ -\dfrac{6\tilde{A}}{\pi\zeta} A_{10} + \left(\dfrac{3}{2} + \dfrac{18\tilde{A}}{5\pi\zeta} \right) A_{01} = 3n\mathcal{D}, \end{cases}$$

where $\tilde{A}$ and $\mathcal{D}$ are given by formulas (63) and (64) respectively, with no dependence on the vibrational levels. Finally, the thermal diffusion D_{Ti} is equal to zero, and the diffusion matrix D_{ik} is given by

$$D_{ik} = -\mathcal{D}, \qquad \text{if } i \neq k, \tag{164}$$

$$D_{ii} = \mathcal{D} \left(\frac{1}{x_i} - 1 \right). \tag{165}$$

The formulas we obtained in the latter case for shear viscosity, bulk viscosity and thermal conductivity are similar to those derived in the monotemperature case. Of course, both approaches are quite different. In the one temperature approach, the thermal conductivity includs the vibrational mode. It is computed assuming a Boltzmann distribution for the population levels. In our case, the vibrational energy transfers are due to diffusion terms containing D_{ik} and allowed us to predict correctely vibrational energy transfers in flow regions where a strong vibrational nonequilibrium occurs.

9 Conclusion

The transport kinetic theory of pure gas developed in the case of strong vibrational nonequilibrium was recalled. The corresponding macrocopic system of equations is given, included the relaxation equations for the population of each vibrational energy levels and the equations of momentum and total energy conservation. General systems are given to compute transport coefficients. Finally simplifications of the previous systems are proposed in order to deduce systems whose solutions may easily be obtained by classical numerical methods.

That work may be generalized to a reacting gas mixture with strong vibrational and chemical nonequilibrium.

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